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Automated Calibration and Analysis of VOCs with a Capillary Column Gas Chromatograph Equipped for Reduced Temperature Trapping

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16. ABSTRACT

Recently an automated system for monitoring volatile organics by reduced temperature (-150°C) preconcentration and capillary column/gas chromatographic analysis has been assembled and evaluated. The automation has now been extended to include multipoint calibration using single stage dilution of trace level organics with humidified zero air. Instructions for automation are carried out under microprocessor control on a Hewlett Packard Model 5880A gas chromatograph using a Basic language program to actuate external voltage outputs that set the electronic flow controllers and solenoid valves in the calibrator hardware. A sixteen-compound mixture of volatile organics has been used to demonstrate a five-point calibration. Data for each compound at each of five concentration levels are stored and used to obtain linear regressions, providing values of slope and intercept for the fit. The slopes are then entered manually via the HP 5880 keyboard into the calibration table. This is an abstract of a proposed presentation and does not necessarily reflect EPA policy. Mention of trade names of commercial products does not constitute endorsement or recommendation for use.

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Introduction

The U.S.E.P.A. through its development program for new and improved instrumentation for monitoring air quality, has sought more sensitive monitoring techniques for individual volatile organics. One approach to increasing sensitivity is to selectively preconcentrate the organics prior to using capillary column, gas chromatographic analysis. In pursuing this goal we have sponsored a research and development activity to evaluate the reduced temperature preconcentration technique. The technique is widely used both for collecting whole air samples at liquid nitrogen temperatures[1] and for selectively trapping volatile organics from flowing sample air with liquid argon or liquid oxygen[2,3]. In preparation for contractual efforts to determine the effect of alternative system designs on trapping efficiency and on sample integrity, we have automated calibration and analysis steps for a VOC monitoring system. Since the parts of the system design related to the preconcentrator and the analysis have been previously discussed[4], the emphasis here is on the design and operation of the automated calibration subsystem.

The overall system design has proved to be invaluable in performing the numerous parameter tests necessary to optimize system performance. This is due to the elimination of a number of tedious manual procedures. In its current form the system can be calibrated and run automatically in unattended operation. This enhances the reproducibility of the monitoring procedure and hence improves the quality of the data. As noted in previous work, the trap temperature can be set from -180°C to +150°C; this feature has been used to investigate the collection efficiency as a function of trap temperature[5]. The system can be used as an on site monitor with hourly printouts documenting VOC concentrations over a fraction of the preceeding hour. Also, remotely collected samples can be analyzed on a centrally located system.

Experimental Methods

Figure 1 shows the overall system schematic. The analytical system consists of a Hewlett Packard Model 5880A gas chromatograph equipped with a capillary column and with both electron capture and flame ionization detectors. Calibration is achieved using a single stage, dynamic dilution of a compressed gas mixture of volatile organic compounds in nitrogen (Scott Environmental Technology, Inc., unanalyzed mixture of 16 VOCs at nominal concentrations of 10 ppmv each) with humidified zero air. The mixture flows through a glass manifold past the inlet to the analytical system. Sample air is pulled into the analytical system through a Nafion tube dryer (Perma-Pure Products, Inc., Model MD250P). As depicted in Figure 1, the sample air is routed through a Model VIII Seiscor valve (high temperature option) and through the trap at a flow rate of 15 cc/min. In this flow configuration, the trap is cooled to -150°C by controlled release of liquid nitrogen so that volatile organics are condensed on the trap surfaces while N_2, O_2 and some other sample components are passed to the pump. After a period of preconcentration (10 -30 min.),

the valve is switched and the trap heated. The carrier gas entrains the thermally desorbed gases and carries them into the GC oven. Details of automation of sampling and analysis are given elsewhere[4].

The gas flow through the calibration system is routed and regulated by a combination of two Tylan Model 260 mass flow controllers, three Mace Corp. 115 actuated Teflon solenoid valves and a needle valve. Under typical conditions using the configuration shown in Figure 1, a low flow rate, 4 cc/min., from FC-L mixes with a high flow rate, 2 L/min., of zero air from FC-H to give approximately 20 ppbv. The three solenoid valves are labeled 8-10 to correspond to circuit contacts (reed relays) on the HP 5880, as shown schematically in Figure 2. Use of the other circuit contacts is described below. Closure of a relay supplies +5 volts dc to a power transistor that in turn completes the 115 volt ac circuit to the corresponding solenoid valve. The reed relays are closed by keystroke command on the 5880 keyboard or, if the system is under program control, by a Basic language program statement. Similarly, any of four fixed dc voltages is available from the HP 5880 to use as a control voltage at one input of the FC-L Tylan unit, as shown in Figure 3. The four dc voltages are set by use of variable resistors and each corresponds to a fixed dilution ratio. Since numbered valve circuits 1-6 on the HP 5880 are designed to supply 24 volts dc and a simple contact closure is all that is needed, the 24 volt signals were used to trigger relays for valve circuits 2, 5 and 6. Continuing redesign efforts include use of a modified commercial calibrator with remote control capability and the use of a fixed set of resisters.

To automate the calibration, a Basic program was developed as part of EPA Contract 68-02-3487 to Battelle Columbus Laboratories. The program consists of approximately 400 lines. It contains previously entered concentrations for compressed gas standards, names for nineteen VOCs for the FID and eight for ECD, and the dilution ratios (four values plus zero) to be used in calibration. Once the program is started, the operator is required to answer a number of questions in order to establish: (1) the type of run, e.g. calibration (single or multipoint) or ambient monitoring (number of runs); and (2) certain timing parameters for the reduced temperature preconcentrator such as collection time, cool-down time, etc. If the calibration mode is chosen, the program then successively steps the calibrator through each of the dilution ratios. A GC analysis occurs for each concentration, during which compounds are identified by retention time and peak areas are recorded in area counts. These data are stored for a subsequent linear regression analysis that occurs under program control. Values of slope, M, and intercept, B, are calculated from the fit for each of the VOCs and printed on the HP keyboard printers, one for each detector. Assuming a zero or at least constant background signal, and response linearity, the M values correspond to response factors in units of ppbv/area count. These values are then entered via the HP 5880 keyboard into the calibration table and subsequently used to obtain a ppbv estimate of unknown samples. The overall calibration procedure consists of five steps as noted below:

1. Obtain compressed gas, multicomponent mixtures of VOCs.

2. Determine GC retention times for each VOC and set up the HP 5880 calibration table using HP format.

3. Use Basic language program to operate auto-calibrator with the HP 5880.

4. Obtain response factors from linear regression analysis, i.e. Y = MX + B where Y denotes ppbv and X denotes peak area counts.

5. Enter M values in HP 5880 calibration table in preparation for an automated monitoring sequence.

An alternate calibrator configuration is shown in Figure 4. This configuration can be used to by-pass the Nafion tube dryer so as to investigate its effect on sample integrity. All valve circuits shown in Figure 2 are used.

Results

The result of a five point calibration is shown in Table I. Provided the M and B values are reasonable and the R^2 (coefficient of determination) values are near unity, the M values are accepted and entered in the HP 5880 calibration table. Values of (N) in Table I indicate the number of calibration levels identified for a component where 5 is the maximum value. An example of the calibration table is shown in Table II. M values are identical with the Amt/AREA (ppbv/ area count) values.

Plots of response versus concentration using a sample collection volume of 150 cc. have been plotted for both FID and ECD outputs. The FID response is linear over the 0-50 ppbv range for all the VOCs measured. However, the ECD response begins to saturate and is nonlinear for certain of the halocarbons. Since ambient level concentrations are expected to be in the low ppbv levels, M values for use with the ECD were often determined by deleting the lower value of calibration concentration. Lower concentration compressed gas standards or a second stage of dilution are needed to avoid this ECD nonlinearity.

The precision of system calibration using the single stage calibrator was characterized in two ways. In the first, six samples were analyzed with the calibrator set for constant dilution at approximately 4 ppbv for the sixteen compounds in the Scott cylinder. Table III lists these compounds in order of retention time on a capillary column with a crosslinked methyl silicone-coated film. No Perma-Pure dryer was used while obtaining the data listed as "Through Calibrator." The average percent relative standard deviation for six replicates using the FID output was 3.8% with a variation from 2.5% for propane and methyl chloroform to 5.8% for the highest molecular weight compound, hexachlorobutadiene. In most cases the sequence of six readings showed a trend due to an obvious conditioning of the system. The second data column in Table III shows the results for a similar analysis of precision obtained by analyzing ppbv concentrations directly from compressed gas cylinders. The average precision of 2.0% is for 4 replicates and implies a higher precision. Based on this and other data, we believe that the precision for measuring a given concentration level is limited by conditioning of the calibrator,

manifold system. Current experimental efforts include the characterization of these conditioning effects.

A second test of the calibrator was to compare five point calibration curves before and after a series of ambient air monitoring runs covering three days. All the compounds listed in Table III were compared in this way. Representative data for carbon tetrachloride and trichloroethylene using the FID are given in Table IV. Statistical analysis of the data consisted of regressing concentration on peak area (PA) and determining the least squares regression line. An estimated concentration $\underline{c}$ is obtained from the formula $\underline{c} = M(PA) + B$, for each calibration curve. Each calibration point (c,PA) has associated with it an estimated concentration $\underline{c}$, an error in estimation $e = \underline{c} - c$ and a percent relative error $(e/\underline{c}) \times 100\%$. Percent relative errors of less than 11% were obtained for both example compounds and similar values were obtained for all but two of the remaining compounds. Benzyl chloride and hexachlorobutadiene were the exceptions, exhibiting relative error values of approximately 20% at the lowest non-zero concentration level. Intercept values were higher and more variable than expected on the basis of FID noise alone. Slope values changed by less than 10% for all compounds over the three day period of ambient runs.

Conclusions

Calibration of a capillary column GC system with a reduced temperature preconcentrator for VOCs has been automated. Calibration hardware is exercised by electrical signals initiated by Basic language programming steps from the internal microprocessor of a HP 5880A gas chromatograph. Replications of analysis of at 4 ppbv using a single stage dilution and FID give an average percent standard deviation of 3.8% for a sixteen compound mixture of VOCs in air. Five point calibration runs before and after ambient air monitoring runs show typically less than 10% drift in slope values and percent relative error values of less than ±11% for concentrations over the range (0 - 50 ppbv). Higher molecular weight compounds have greater variability at constant concentrations and higher relative errors with respect to five point linear regression analysis. This and higher-thanexpected intercept values imply possibilities for better precision by adjustment of the temperature profile that the sample encounters in passing through the system. This adjustment is expected to reduce sample adsorption and the attendant memory effects.

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TABLE I. SAMPLE PRINTOUT AFTER MULTIPOINT CALIBRATION

Electron Capture Detector
For Y = MX + B

Compound	Slope, M (ppbv/area ct.)	Offset, B (ppbv)	R Squared (N)*
Trichlorotri-Fluoroethane	2.62546E-04	0.79840E-01	.999716 (5)
Chloroform	6.34828E-04	-5.18378E-01	.999691 (5)
Methyl-Chloroform	2.18761E-04	-7.81026E-01	.998684 (5)
Carbon Tetrachloride**	0.40958E-04	-0.06032E-01	.999888 (4)
Trichloro-Ethylene	4.70383E-04	-8.25398E-01	.999237 (5)
1-2 Dibromo-Ethane	3.49673E-04	-7.16019E-01	.999412 (5)
Tetrachloro-Ethylene	0.87779E-04	-8.57338E-01	.997217 (5)
Hexachloro-Butadiene**	0.54436E-04	-4.29442E-01	.998655 (4)

*N denotes number of points identified and used for regression.

**Corrected for nonlinear response at high concentrations.

TABLE II. EXAMPLE OF A CALIBRATION TABLE PRINTOUT FROM THE HP 5880A

Calib Table:

Cal	RT*	Level	Amt (ppbv)	Amt/Area (ppbv/area ct.)	Name
1	10.13	1	1.00000E+04	2.62546E-04	C2Cl3Fl3
2	12.20	1	1.00000E+04	6.34828E-04	Chloroform
3	13.03	1	1.00000E+04	2.18761E-04	Mechloroform
4	13.58	1	1.00000E+04	0.40948E-04	CCl4
5	14.50	1	1.00000E+04	4.70383E-04	Triclene
6	16.89	1	1.00000E+04	3.49673E-04	1, 2 Bro-Ethan
7	17.43	1	1.00000E+04	0.87779E-04	Perclene
8	26.03	1	1.00000E+04	0.54435E-04	C4Cl6

*RT denotes retention time on the GC column.

TABLE III. PRECISION OF VOC ANALYSIS ON FID - DIRECT ANALYSIS VS ANALYSIS THROUGH CALIBRATOR

Compound	Percent Relative Standard Deviation	
	Through Calibrator*	Direct**
Propane	2.5	
Vinyl Chloride	4.0	1.1
Vinylidene Chloride	2.7	
Trichlorotrifluoroethane	4.8	0.6
Chloroform	3.6	2.7
1, 2 Dichloroethane	3.1	
Methyl Chloroform	2.5	
Carbon Tetrachloride	3.0	1.9
Trichloroethylene	3.8	
1, 3 Dichloropropene (cis)	2.8	
1, 3 Dichloropropene (trans)	4.6	
1, 2 Dibomoethane	2.9	
Tetrachloroethylene	4.9	1.7
Chlorobenzene	4.1	1.9
Benzyl Chloride	5.3	
Hexachlorobutadiene	5.8	
Average Value	3.8	2.0

*Calibrator used for dilution to 4 ppbv, except for 1, 3 Dichloropropene, cis- and trans- which were 2 ppbv.

**Direct analysis form compressed gas tank.

TABLE IV. EXAMPLE OF RESULTS OF PRE-RUN AND POST-RUN CALIBRATION FOR CARBON TETRACHLORIDE AND TRICHLOROETHYLENE

Regression Equation	Calibration Status	Conc (ppbv)	Raw Area	Estimated Conc	Error (ppbv)	% Relative Error
Carbon Tetrachloride						
c = 0.39 + 3.09 (PA)	Pre-Run	0.00	0.00	0.39	-0.39	—
		4.04	1.09	3.75	0.29	7.1
		9.90	3.05	9.80	0.10	1.0
		19.80	6.27	19.74	0.07	0.3
		49.30	15.87	49.36	-0.06	-0.1
c = 0.42 + 3.31 (PA)	Post-Run	0.00	0.00	0.42	-0.42	—
		3.88	1.14	4.20	-0.32	-8.2
		10.10	2.73	9.47	0.64	6.3
		20.00	5.82	19.69	0.31	1.6
		50.40	15.16	50.61	-0.21	-0.4
Trichloroethylene						
c = 0.54 + 0.76 (PA)	Pre-Run	0.00	0.00	0.54	-0.54	—
		4.04	4.32	3.84	0.02	5.0
		9.90	11.98	9.68	0.22	2.3
		19.80	24.89	19.52	0.28	1.4
		49.30	64.16	49.46	-0.16	-0.3
c = 1.15 + 0.79 (PA)	Post-Run	0.00	0.00	1.15	-1.15	—
		3.88	3.49	3.90	-0.02	-0.6
		10.10	9.96	9.00	1.10	10.9
		20.00	23.42	19.61	0.39	2.0
		50.40	62.90	50.72	-0.32	-0.6

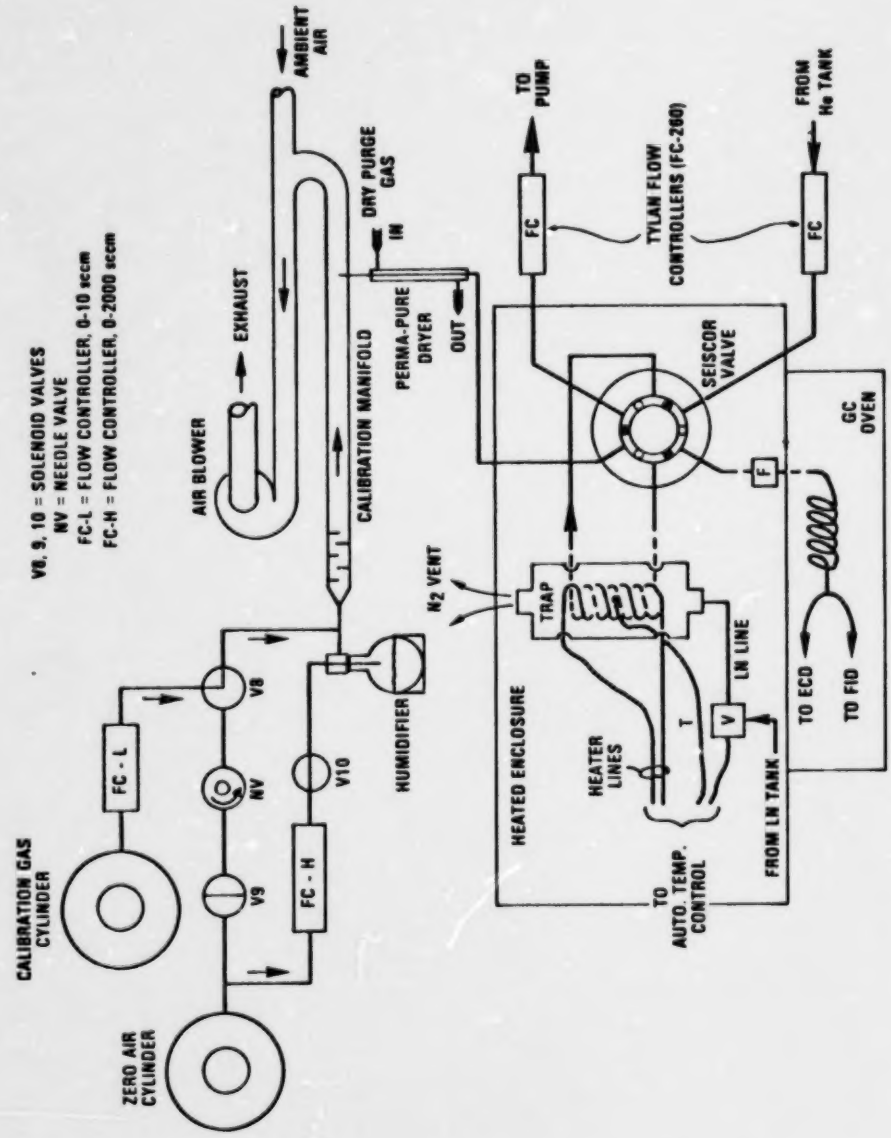


Figure 1. Functional schematic of system for VOC analysis. V denotes valve; T, thermocouple; F, low volume fitting.

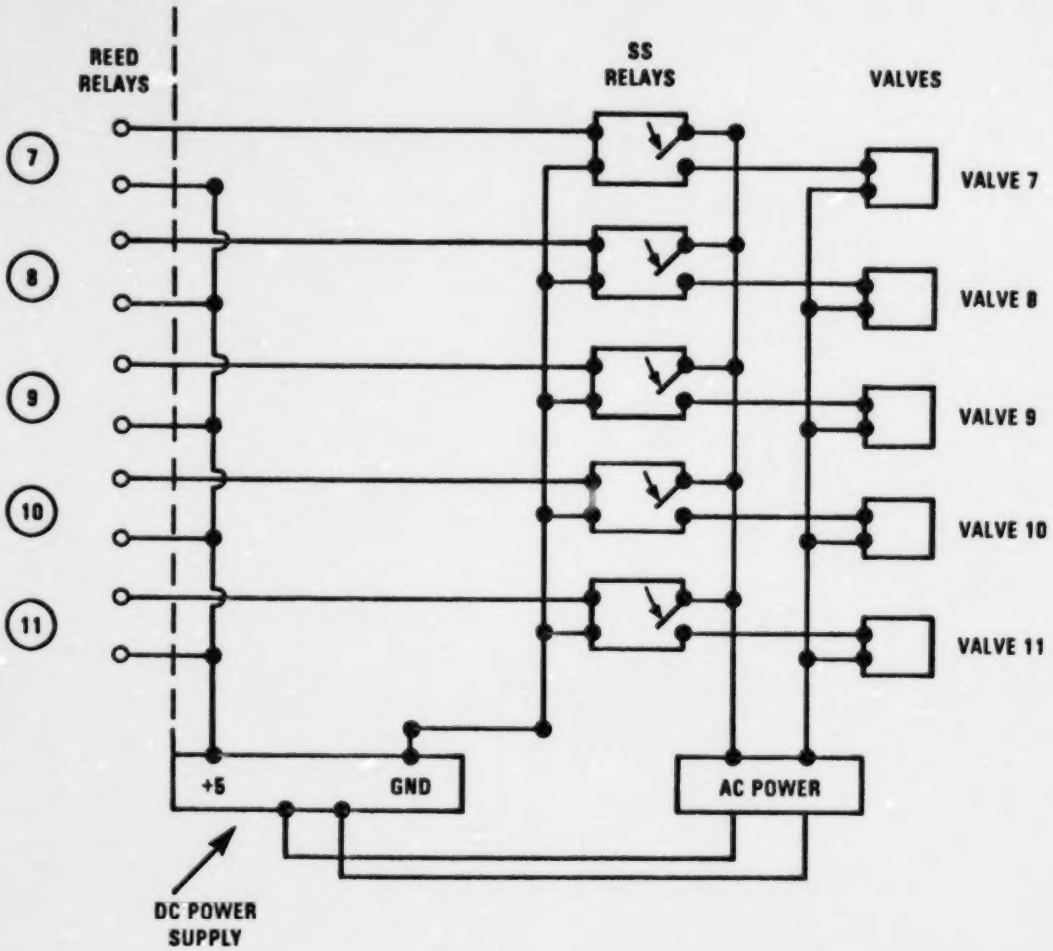
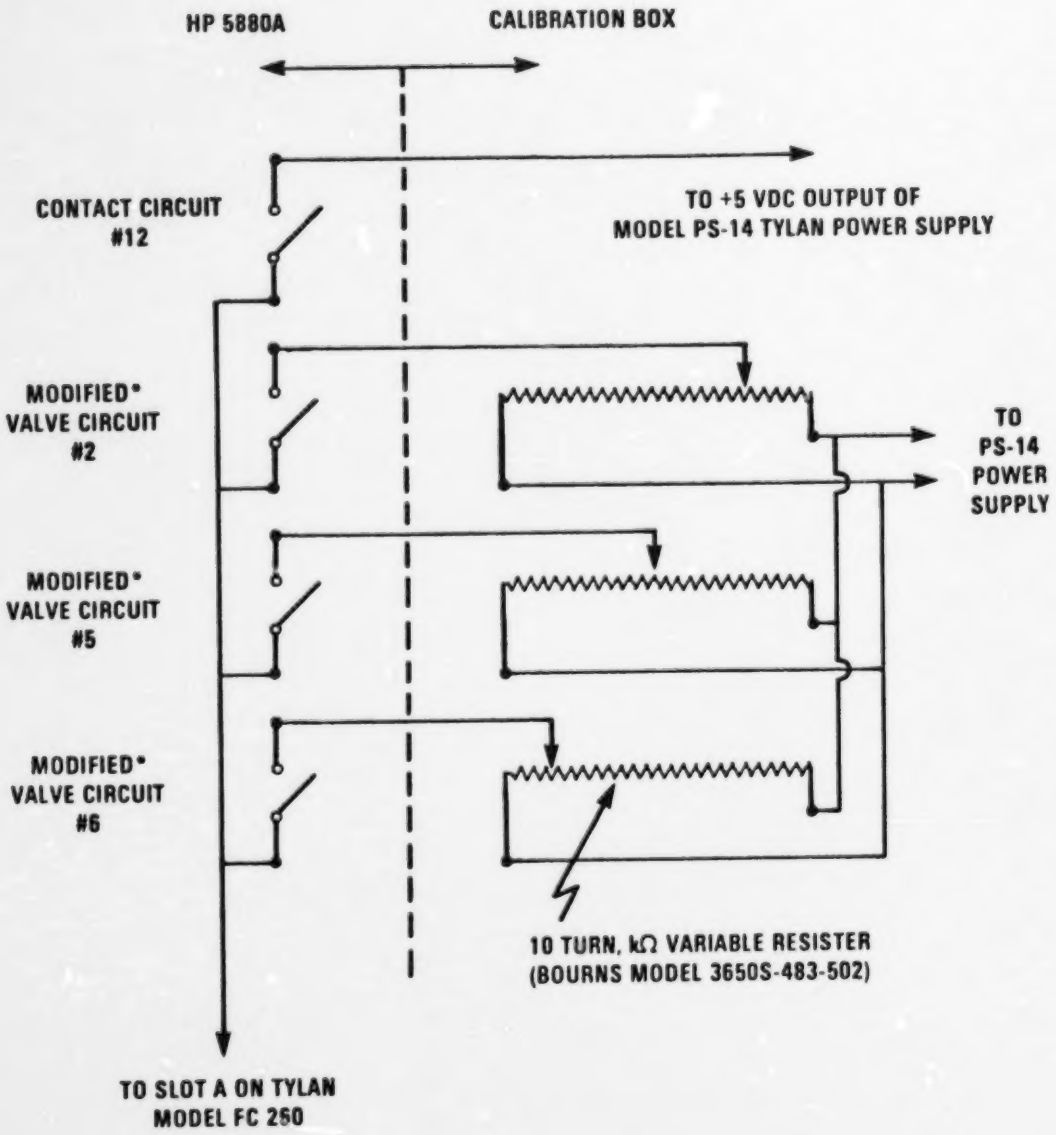


Figure 2. Electrical schematic of solid state relay interface between HP 5880 reed relays and solenoid values.


HP 5880A
CALIBRATION BOX
CONTACT CIRCUIT #12
TO +5 VDC OUTPUT OF MODEL PS-14 TYLAN POWER SUPPLY
MODIFIED* VALVE CIRCUIT #2
TO PS-14 POWER SUPPLY
MODIFIED* VALVE CIRCUIT #5
MODIFIED* VALVE CIRCUIT #6
10 TURN, kΩ VARIABLE RESISTER (BOURNS MODEL 3650S-483-502)
TO SLOT A ON TYLAN MODEL FC 250

* MODIFICATION OF HP CIRCUITS TO PROVIDE A SIMPLE CONTACT CIRCUIT.

Figure 3. Electrical schematic for changing control voltage (and flow rate) on FC-L.

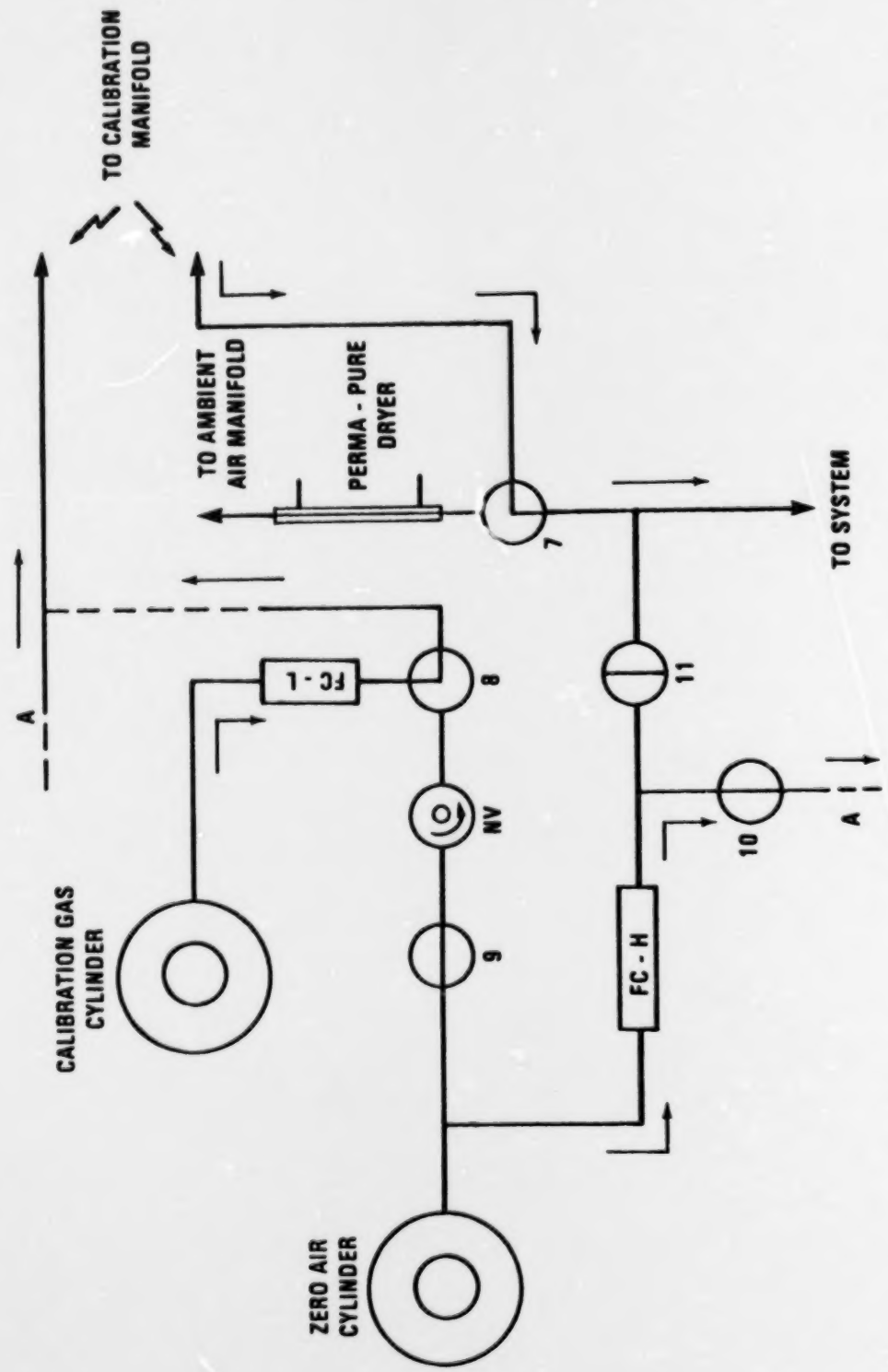


Figure 4. Alternative single stage dilution scheme, see Figure 1 for symbols.